Industrial Crystallization of Organic Compounds

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Fundamentals and industrial applications of crystallization of organic compounds are reviewed. The methods to upgrade organic products in terms of its purity and its morphology are introduced. How crystallization of organics can be useful in producing ultra-pure materials are also described.

INTRODUCTION

The development of the chemical process industries has accounted also for the increasing requirements concerning both quality and physical properties of the final products. In recent years in particular, emphasis has been placed on product quality like its purity and shape and size of crystals, and economic aspects. One of the fundamental operations in the final treatment of chemical products is the process of crystallization. The quality components are strongly influenced by the geometry and type of crystallizer, the operating conditions, and the properties of the liquid and solid phases[1]. Thus, the use of crystallization in industrial practice is to recover pure material from impure mixtures due to unprecedented selectivity and to produce a specified structure of solids due to its ability to form and develop particle[1-5]. Although much literature exists on the crystallization of inorganic commodity chemicals, until recently the same level of interest has not been devoted to the crystal growth of organic materials. In addition, the study of organic crystallization is a multidisciplinary area with chemical engineer, organic solid-state chemists, pharmaceutical scientists, and physicists all involved. However, the technology of industrial crystallization looks certainly more like an art than the technical aspects. In this paper, fundamentals and crystallization processes to upgrade organic materials are reviewed and the mechanisms of crystallization are discussed from chemical engineering point of view.

SEPARATION/PURIFICATION OF ORGANIC COMPOUNDS

Fractional crystallization is a general term for separation processes which can be used for large scale separation and ultrapurification of organic compounds from multicomponent mixtures in an economically favorable and environmentally safe way[6]. The driving force for crystallization is either cooing or pressurization. The processes of fractional crystallization can be characterized as a multistep operation which usually involves a countercurrent contact between crystal and mother liquor in such a way that the crystals are grown and/or washed in mother liquor of increasing purity at ascending temperatures. Figure 1 shows the general set-up of fractional crystallization processes.
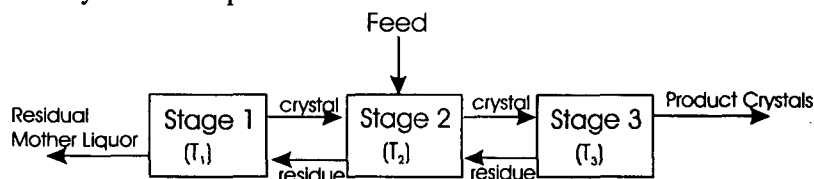

Figure 1. General set-up of fractional crystallization processes

Advantages of fractional crystallization in comparison to conventional separation techniques like distillation and extraction are its superior selectivity, lower energy consumption and

moderate operating conditions whereas addition of toxic or explosive solvents can usually be avoided. There are two types of industrial crystallization methods : crystallization of solution and melt crystallization. Solution crystallization is used for separation of mixtures as well as upgrading of crystal morphology, classified into adductive crystallization, extractive crystallization, reaction crystallization, etc. Melt crystallization is used for separation of organics. Table 1 summarizes the differences between melt and solution crystallization.

Table 1. Differences between melt and solution crystallization

Melt crystallization	Solution crystallization
Higher operating temperature	Lower operating temperature
Good selectivity	Better selectivity
Higher viscosity fluid	Lower viscosity fluid
Moderate growth rate	Higher growth rate
Compact equipment	Larger equipment
No solvent recovery	Solvent recovery required
Reduced environmental hazard	Possible environmental hazard

Melt Crystallization

Melt crystallization is one of the separation techniques applied in the separation of organics(such as close boiling hydrocarbons), isomers, heat sensible materials and so on[3,6]. The use of melt crystallization for separation of organic mixtures has increased rapidly in the chemical industry over the past few years. In melt crystallization the impurities are recovered in molten form and can be cycled, incinerated, or treated in some other fashion without an intermediate solvent removal step. From this point of view, melt crystallization is a clean technology for the separation of organics without using a solvent. The chemical process industries are beginning to focus on manufacturing processes that address an enhanced environmental awareness on the part of public and more stringent government regulations for chemical disposal and emissions. Unit operations that minimize solvents and reduce operator exposure to chemicals are needed in today's chemical industries. An example of currently available technology is melt crystallization which offers unique separative potential for problematic and high-purity applications in addition to environmental and health benefits.

There are two different types in melt crystallization ; one of these applies a cold surface on which a crystal layer is produced from the stable melt and the other employs a simple stirred vessel in which a crystal suspension is produced by cooling the entire melt. For recovering the crystals formed, the former uses a temperature gradient technique or a mechanical device, and the latter uses subsidiary equipment such as filters and centrifuges. Layer growth and suspension crystallization are usually operated batchwise whereas suspension crystallization mostly feature a continuous operation.
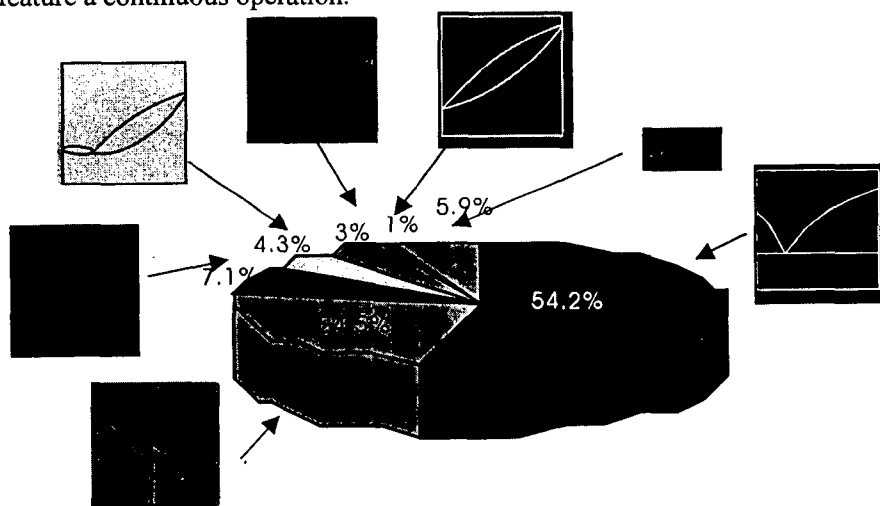

Figure 2. Phase diagrams of binary organic mixtures

Figure 2 shows the data reviewed with 85.9% of the binary organic mixtures. About 60% of all organic mixtures for which phase diagrams can be found are eutectic systems. Further 32% belong to the group of molecular forming compounds and systems with peritectic and eutectic points. Only 14.1% of all substances belong to the group of solid-solution forming substances. In addition, most organics have melting points that are relatively low. Figure 3 shows melting points of common organics. Over 70% of these compounds have a melting point in the range of 0-200°C, and can be separated by melt crystallization. Therefore these materials can be economically separated and ultrapurified by crystallization technologies. Due to the increased demand for ultrapure materials and energy saving, the solvent-free melt crystallization technologies gained more importance in recent years.

In comparison with other separation technologies, e.g. distillation, the required energy for the phase change liquid/solid is much lower. This is due to the relatively low level of temperature and the much smaller latent heats. The energy required for the phase transition liquid/solid is only about 1/3 to 1/7 of the gas/liquid phase transition energy. Due to the low temperature level it is also possible to treat heat sensitive substances, like foods or polymer. The separation technique of melt crystallization does not need any additional substances like solvent, e.g. in extraction. No further impurities get into the substance to be purified and no chemicals(solvent) have to be generated. So in comparison with extraction solvent recovery, capital and energy costs can be saved.
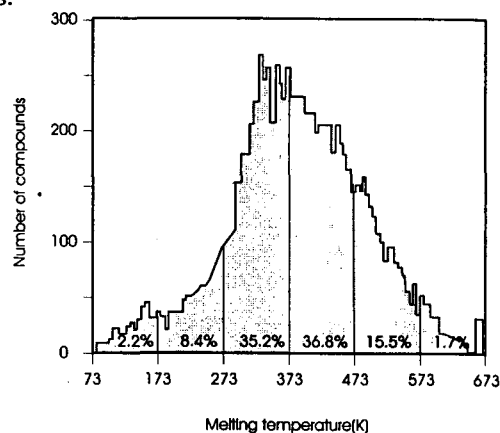

Figure 3. Melting points of common organic compounds

Purification mechanisms

Crystal purity is hampered by impurities,which are incorporated in the crystal lattice, included in the crystal matrix, and/or adhered to the crystal surface. Several purification mechanisms can be applied to upgrade the crystal purity and thus to improve the overall separation efficiency of crystallization process. Usually four purification mechanisms are distinguished : washing, sweating, recrystallization and solid state diffusion[4,7]. Figure 4 shows an example of purification by sweating. The purity of crystals used is about 96.9 wt% n-dodecanol. As the mass fraction of crystals melted out increases, higher purity crystals can be obtained.
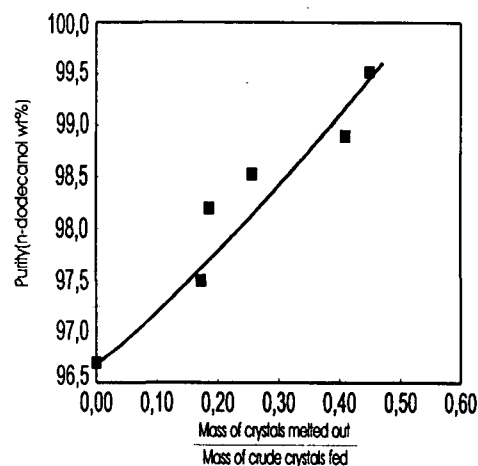

Figure 4. Purification of organic crystals

According to Wintermantel[6], the purity of crystals is the function of the crystal growth rate G and mass transfer coefficient k_d and decreases with increasing growth rate G but increases with increasing mass transfer coefficient k_d.

$$\text{Purity} = f\left(\frac{\rho_l - c_l}{c_l} \cdot \frac{k_d}{G} \cdot \frac{\rho_l}{\rho_s}\right)$$ (1)

To characterize the efficiency of a melt crystallization process, the effective distribution coefficient, k_{eff}, is defined as the ratio of the impurity concentration in the crystal phase to the

impurity concentration in the melt phase:

$$k_{eff} = \frac{x_C}{x_R} \qquad (2)$$

A k_{eff} close to 1 means almost no separation, in contrary a k_{eff} of 0 means perfect separation. Figure 5 shows, as already described above, the influence of the growth rate G on the effective distribution coefficient k_{eff}. As a comparison, with results obtained from layer crystallization[2,7], shows, the effective distribution coefficients for a growth rate of 0.5×10^{-6} m/s are in the suspension process smaller than for the layer crystallization process. Results from the experiments show also a decrease of the distribution coefficient for using a sweating process.
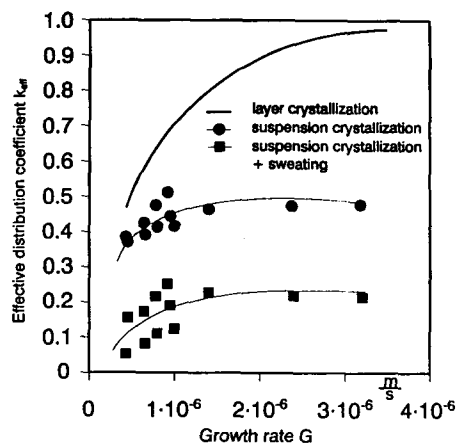

Figure 5. k_{eff} versus G

Extractive Crystallization

A third component is added to the two components to modify the solid-liquid phase behavior. This extraneous agent does not form a solid phase at any point in the process. Findly et al.[8] describe in detail an extractive crystallization process in which para-xylene and meta-xylene are completely separated from each other by using n-heptane as the extractive solvent. Many organic mixtures with its isomer were separated by extractive crystallization. An example of the process to separate organic isomer is shown in Figure 6[9].
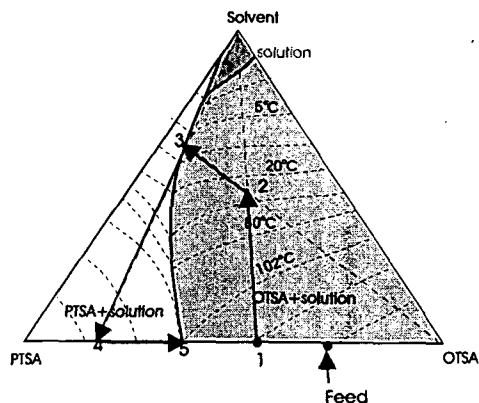

Figure 6. Extractive crystallization

Adductive Crystallization

An adduct - a crystalline solid phase is formed by adding a third component to the mixture. This chosen agent should form an adduct with one of the components in a selective manner. The adduct formed is subsequently separated and then dissociated, usually by means of heat, to recover the component from the extraneous component. Host compounds used in adductive crystallization are urea, thiourea, Werner complex, cyclodextrin, etc.

Urea forms adducts with straight-chain paraffins, but thiourea forms adducts with branched-chain paraffins or naphthenic hydrocarbons since the cage diameters of urea and thiourea are about 5.1 Å and 6.5 Å, respectively. Thiourea as the adduct-forming compound in the separation of polymethylbenzenes, in the separation of naphthen mixtures, and in the separation of dimethylethylbenzenes was successfully used[5,10,11,12]. Figure 7 is a distorted-scale schematic of the phase diagram measured for naphthen-thiourea-methanol system. In the region ABCA, adduct exists with liquid and is easily separated from liquid by phase separation.
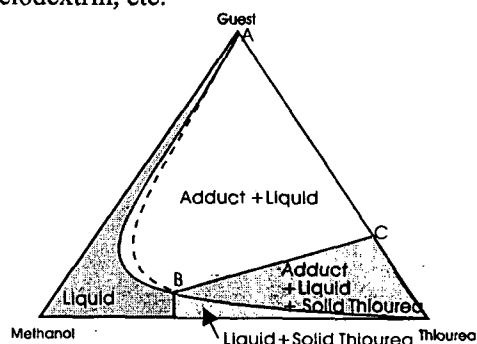

Figure 7. Adductive crystallization

KINETICS OF CRYSTALLIZATION

The kinetics for crystal growth and nucleation are needed in the design of crystallization equipment and in the control of crystal morphology for industrial crystallization. Table 2 lists the empirical kinetic equations to be commonly used for these[1,5,12].

Table 2. Kinetic equations

Maximum allowable supersaturation :	$\Delta C_{max} = (dC^* / dT)\Delta T_{max}$
	$\log b = (n-1)\log\dfrac{dC^*}{dT} + \log k_n + n\log\Delta T_{max}$
Nucleation rate :	$B = k_n\Delta C^n = k_n\Delta C_{max}{}^n$
Crystal growth rate :	$G = k_g(\Delta C)^g$
Mass transfer coefficient :	$N_{Sh} = a + b(N_{Re})^{1/2}(N_{Sc})^{1/3}$
Heat transfer coefficient :	$N_{Nu} = \alpha + \beta(N_{Re})^{1/2}(N_{Pr})^{1/3}$

CONTROL OF CRYSTAL MORPHOLOGY

Calculation of crystal size

The mean size and size distribution of crystals are important parameters in production of organic crystals and in the separation of crystals from mother liquor because they determine both the surface area to be washed and the rate of filtration.

They are complex functions of nucleation and growth, which are functions of process variables such as agitation rate, feed composition, and production rate. These functions are eventually related to the degree of supersaturation. Crystal size depends on the growth rate G, the nucleation rate B, and holdup of crystal φ_s[14,15].

$$\overline{L} = f\left(\frac{G\varphi_s}{B}\right) \qquad (3)$$

This relation results from the fact that the mean crystal size increases with an increasing growth rate and holdup of crystal and a decreasing nucleation rate. Figure 8 shows the comparison between mean crystal sizes calculated from estimation of parameters in equation 3 and obtained experimentally[14].
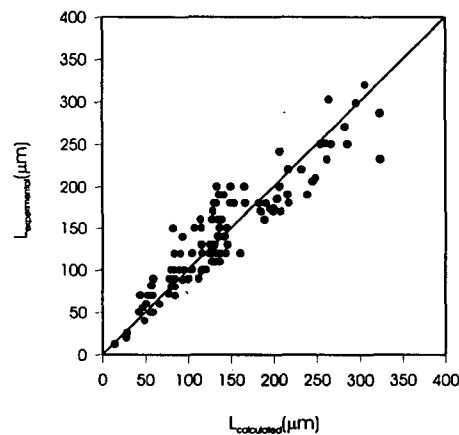

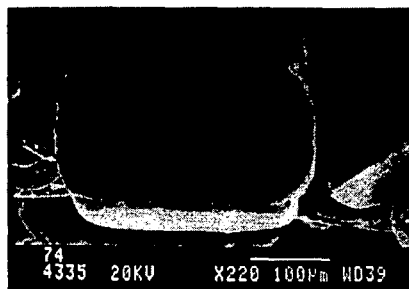Figure 8. Expectation of crystal size

Shape of crystals

It is extremely difficult to predict the shape of crystals, because there is a vast variety of different parameters. When dealing with industrial crystallizer, the shape of crystals can be influenced by the properties of the crystalline solid like lattice, morphology, hardness, strength, etc., the properties of the solution like pressure, temperature, density, viscosity, supersaturation, etc., and the operating mode and conditions like specific power input, suspension density, operation time, etc.

With respect to the kinetics and mechanisms of crystals, the shape of crystals will be influenced by the different growth rate of each crystal faces due to the adsorption of impurities, admixtures and additives, agglomerations of crystals, attrition of crystals, and breakages. Figure 9 shows organic crystals crystallized in water under right operating conditions from the crude crystals coming from reaction process which have a jagged rod-like shape[15].

Selecting an appropriate operation of crystallizer is thought to be very important to control morphology of crystals.
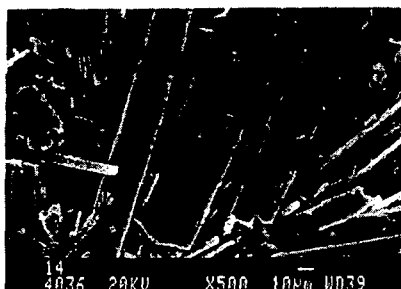
(Crystals after reaction)   (Crystals after crystallization)

Figure. 9. Control of morphology

NOMENCLATURE

B	Nucleation rate
ΔC	Supersaturation
ΔC_{max}	Maximum allowable supersaturation
G	Crystal growth rate
k_d	Mass transfer coefficient
k_g	Growth rate constant
k_n	Nucleation rate constant
k_{eff}	Effective distribution coefficient
L_{50}	Median particle size, m
x_c	Concentration of impurities in the crystal
x_R	Concentration of impurities in residual melt

REFERENCES

1. A. Mersmann, 1994, Crystallization Technology Handbook, Marcel Dekker, Inc.,N.Y.
2. S. J. Jancic, 1986, The Sulzer MWB Fractional Crystallization System, Techncal Review Sulzer, Winterthur, Switzerland
3. K. J. Kim, and A. Mersmann, "Melt Crystallization with Direct Contact Cooling Techniques", Chem. Eng. Res. Des., 75(Part A), 176 - 182(1997).
4. K. J. Kim and A. Mersmann, "Separation of Organics by Melt Crystallization with Direct Contact Cooling", Separation Science & Technology 31(13), 1589-1875 (1996)
5. K. J. Kim, J. M. Lee and S. K. Ryu, Crystal Growth in Thiourea Adduction with Cyclohexane - Methylcyclopentane System , Separations Technology, 6(3), 211-218 (1996).
6. K. Wintermantel and Wellinghoff, G., Melt Crystallization - Theoretical Premises and Technical Limitation, Inter. Chem. Eng., 34(1): 17 - 27(1994).
7. J. Ulrich ,Bierwirth J., Henning S., 'Solid Layer Melt Crystallization', Separation and Purification Methods , 25 1, 1-45 (1996).
8. R. A. Findly and Weedman, J.A., Separation and Purification by Crystallization, Advances in petroleum Chemistry and refining, Interscience, New York, 1, 119(1958).
9. K. J. Kim et al., Separation of isomers with TSA and TSC and its processes, Korean Patent 96-30412(1996).
10. K. J. Kim, J. M. Lee and S. K. Ryu, Separation of Pseudocumene from Naphtha Cracking Raffinate by Thiourea Adduction, Separations Technology., 5(4), 187-195 (1995).
11. K. J. Kim and C. H. Lee and S. K. Ryu, Kinetic Studies in Thiourea Adduction with Cycloheane-Methylcyclopentane System, Ind. Eng. Chem. Res., 33(1), 118 ~ 124   (1994).
12. C. H. Lee, K. J. Kim and S. K. Ryu, Separation of Nonaromatic C6 Compounds from Naphtha Cracking Raffinate by Adductive Crystallization, J. of Chem. Eng. Japan, 25(5), 585 ~ 591 (1992).
13. K. J. Kim, and S. K. Ryu, Nucleation of Thiourea Adduct Crystal with Cyclohexane-Methylcyclopentane, Chem. Eng. Comm. 159(1), 51 ~.66(1997)
14. K. J. Kim et al., "Control of size and shape of NTO crystals in cooling crystallization", CGOM 4, Bremen, 169-174(1997).
15. K. J. Kim et al., Solubility, Density and Metastable Zone Width of NTO + Water System, J. Chem. Eng. Data, in print(1997)